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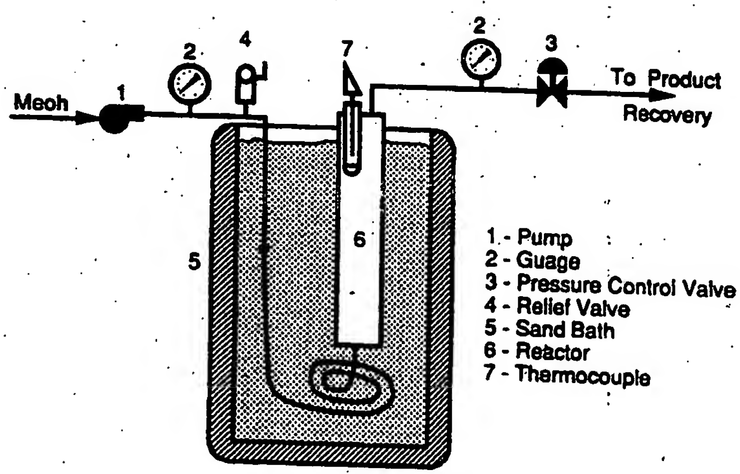
(54) **Recovery of methyl esters of aromatic acids and glycols from thermoplastic polyester scrap.**

(57) Dimethyl terephthalate vapor and glycol vapor are prepared by treating polyester polymer with excess methanol vapors at a temperature above 230 °C. The excess methanol acts as a carrier gas for the dimethyl terephthalate and the glycol.

FIG. 1



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FIELD OF THE INVENTION

This invention relates to the recovery of methyl est rs of aromatic acids such as dimethyl terephthalat and glycols such as ethylene glycol from thermoplastic polyester scrap by treating the scrap with excess methanol vapor at high temperatures.

BACKGROUND OF THE INVENTION

Processes for the recovery of dimethyl terephthalate and ethylene glycol from waste polyester are known. See, for example, U.S. Patents 3,776,945, U.S. Patent 3,488,298 and U.S. Patent 2,884,443. In the '945 patent polyester waste is treated with methanol to form dimethyl terephthalate, the excess methanol is then vaporized and then the dimethyl terephthalate and ethylene glycol are vaporized. The '298 patent depolymerizes polyester by treating it with methanol, then adding phosphorus compound, and finally vaporizing the methanol, ethylene glycol and dimethyl terephthalate. The '443 patent depolymerizes polyester by heating the polyester to a temperature below 210°C in the presence of methanol, a re-esterification catalyst, and a high boiling organic liquid. The dimethyl terephthalate is separated as crystals from the reaction vessel.

SUMMARY OF THE INVENTION

The process of the present invention is for the preparation of dimethyl terephthalate from polymers of terephthalic acid and a glycol, which comprises treating said polymers in a reaction zone with methanol vapor at a temperature above 230 degrees c and at a pressure below about 15 atmospheres, continuously removing vapors of methanol, dimethyl terephthalate, and the glycol from the reaction zone, said vapors containing at least about 3 moles of methanol for every mole of dimethyl terephthalate, separating methan l from said vapors, and separating dimethyl terephthalate from the vapors.

DESCRIPTION OF THE DRAWING

The drawing is a view, partly in cross-section of a reactor suitable for carrying out the process of the invention.

DETAILED DESCRIPTION

The present invention is based on the discovery that polyester resin can be depolymerized by methanol vapor heated to above the critical temperature, i.e. 230°C and that the resulting monomers, dimethyl terephthalate and the glycol, usually ethylene glycol, can be swept continuously from the reactor as vapors along with methanol vapor if the methanol is present in the vapors removed from the reactor in an amount of at least 3 moles of methanol for every mole of dimethyl terephthalate. (The term "critical temperature" is used in its usual technical sense: that is 230°C in the temperature at which it is not possible to liquify methanol by increasing the pressure). The vapors from the reactor are then separated by condensation in a separation column, or cooled and the crystallized dimethyl terephthalate separated, for example, by filtration.

The excess methanol vapor fed to the reactor, aids in the removal of the dimethyl terephthalate vapor from the reactor by acting as a carrier gas. It is preferred that the vapor leaving the reactor contain at least about 5 moles of methanol per mole of dimethyl terephthalate, and mole ratios as high as 100 moles of methanol to one mole of dimethyl terephthalate have been demonstrated as useful.

In addition to polyester containing ethylene glycol, polymers containing units of butylene glycol can be depolymerized and the monomers recovered by the process of this invention.

It is not necessary that the polyester polymer that is treated by the present process be free from contaminants. The process works well on blend of polyester fibers with other fibers such as cotton, polyester that is metallized, polyester that is dyed, polyester that is pigmented, polyester that is mixed with other plastics, etc.

If desired the reactor may also contain solvent for the polyester. As shown in Run 13 below, a suitable solvent is a mixture of methylhydrogenterephthalate and dimethyl terephthalate. Other solvents such as diphenyl, diphenyl ether, diphenylmethane may make it possibl to run the process efficiently at somewhat lower temperatures than the t mperature employed if no solvent is employed. In the absence of s lvent the temperature of the reactor is usually maintained above the melting p int of the polyester. The temperature

is in any case always above the critical temperature for methanol, of 230°C. Th pressure in the reaction vessel is usually maintained between 1 and about 15 atmospheres. Pressures of about 4 to 10 atmospheres are preferred.

The process does not require the use of d polymerization catalysts, and thus avoids the introduction of one or more ingredients that would subsequently have to be removed or neutralized if the monomers were to be again polymerized.

EXAMPLES

The depolymerizations were carried out in the apparatus shown in the Figure. The reactor 6 was charged with the polyester shown in the table and placed in a pre-heated sand bath 5. Methanol flow was started via pump 1. The pressure was measured using gauges 2. The temperature measured by thermocouple 7. The incoming line had a pressure relief valve 4, and the exit line had a pressure control valve 3. At the end of the run the total reactor effluent was weighed and the ester and available glycol content determined. The reactor was cooled, dissembled and the amount of residue determined. The results of the depolymerization of polyethylene terephthalate from varied sources is shown in the table.

TABLE

Source of poly(ethyleneglycol) terephthalate (PET)	RUN	TEMP. (C)	PRES. (PSIG)	PRODUCT (1) MHET(2)	DMT(3)	EG(4)
Co-mingled green bottle waste (80% PET, 20% high density p lyethylene)	1	260	80	2	75	80
	2	280	90	1	85	88
Fl or clippings, (60-40 PET-cotton)	3	260	110	4	83	92
	4	280	100	2	82	89
	5	300	95	4	88	90
Magnetic tape containing ir n and chromium oxides	6	260	110	5	88	90
	7	280	100	5	85	85
Polyvinylidine chloride coated PET film	8	260	65	6	84	90
	9	300	60	8	82	90
M tallized PET film	10	270	60	4	86	80
Photoresist coated PET	11	280	65	7	84	91
PET Oligomer having a degree of p lymerization of 2.	12	260	85	6	84	94
Clear PET and 25% solvent(5)	13				95(6)	88(7)

(1) Per-cent yields based on PET content of the starting material.
(2) Methyl(2-hydroxyethyl)terephthalate
(3) Dimethylterephthalate
(4) Ethylene glycol
(5) 20% Methyl hydrogenterephthalate and 80% dimethylterephthalate.
(6) Based on Total Terephthalate.
(7) Based on PET.

Claims

1. A process for the preparation of dimethyl terephthalate from polymers of polyolefin terephthalat , which comprises treating said polymers in a reaction zone with methanol vapor at a temperature above 230 degrees C continuously removing vapors of methanol, dimethyl terephthalate, and an olefin glycol from the reaction zone, said vapors containing at least about 3 moles of methanol for every mole of dimethyl terephthalate; separating methanol from said vapors, and recovering dimethyl terephthalate.

2. The process of claim 1 in which the methanol is separated from the vapors exiting the reaction zone by condensation, and the dimethyl terephthalate is recovered by condensation.

3. The process of claim 1 in which the reaction zone also contains a solvent for the polyolefin terephthalate.

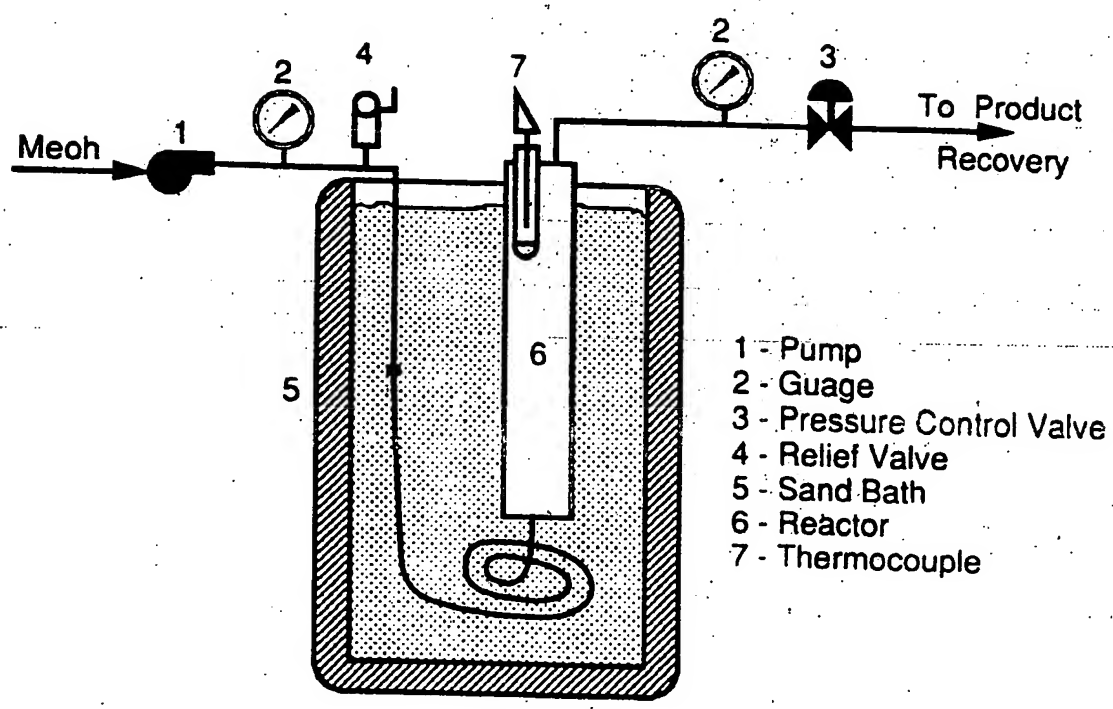
4. The process of claim 1 in which the glycol is ethylene glycol.

5. The process of claim 1 in which the polyolefin terephthalate is treated with methanol vapor at a pressure below about 15 atmospheres.

6. The process of claim 5 in which the pressure is between 1 and 15 atmospheres.

7. The process of claim 2 in which the glycol is also recovered by condensation.

FIG. I


Meoh
1
2
4
7
2
3
To Product
Recovery
6
5
1 - Pump
2 - Guage
3 - Pressure Control Valve
4 - Relief Valve
5 - Sand Bath
6 - Reactor
7 - Thermocouple